Properties and Applications of Rhenium and Its Alloys

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THE PROPERTIES OF RHENIUM

The element rhenium (Re) is a refractory metal that has gained significant recognition as a high-performance engineering material because it exhibits an exclusive combination of properties. Rhenium has the second highest melting point of all metals (after tungsten (W)), the third highest Young's modulus (after iridium (Ir) and osmium (Os)), and the fourth highest density (after Os, Ir and platinum (Pt)). It also has one of the highest strain hardening exponents of all elements, a low coefficient of friction, and a high hardness, all of which result in excellent wear properties. Compared to the other refractory metals, Re has superior tensile strength and creep-rupture strength over a wide temperature range (up to approximately 2000°C). For example, between room temperature and 1200°C, its strength is approximately twice that of W. In addition, the rupture strength of rhenium is greater than that of W at temperatures as high as 2800°C. At 2500°C its strength is comparable to that of carbon composites. These properties imply that structures made of Re have excellent mechanical stability and rigidity, and they enable the design of parts with thin sections. It can also be concluded that Re is extremely attractive for high-temperature structural and energy system applications. A summary of properties is provided in Table 1.

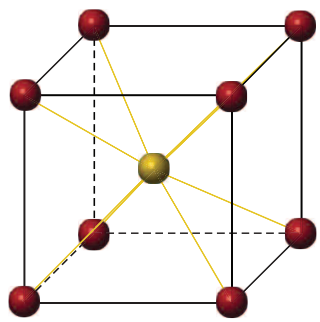

Figure 1. **Illustration of a body-centered cubic structure.**

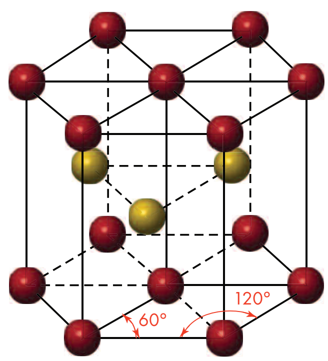

Figure 2. **Illustration of a hexagonal close-packed structure.**

Interestingly, while the other refractory metals have a body-centered cubic (BCC) structure (Figure 1), Re has a hexagonal close-packed (HCP) structure (Figure 2). Consequently, it does not possess a ductile-to-brittle transition and, therefore, can safely be used at subzero temperatures.[1-5]

Rhenium is the only refractory metal that does not form carbides. Even so, the solubility of carbon in Re is relatively high along with the wettability* between these two elements. This combination of properties yields excellent bond strength between these two elements, and indeed, Re is used in contact with graphite and carbon composites, for example in high-temperature rocket engines and hot gas valves.

Rhenium is resistant to a wide range of harsh environments. It is highly resistant to corrosion in hydrochloric and sulfuric acids as well as in seawater. It also has low permeability to hydrogen and resists degradation in hydrogen and inert atmospheres at elevated temperatures. Re is immune to most combustion gases, with the exception of oxygen. On the other hand, Re is readily dissolved in nitric acid and other oxidizing acids. Moist air above 600°C also leaves Re vulnerable to oxidation due to the formation of Re_2O_7. Hence, oxidation protection is often sought through the development of Re alloys and the application of an oxidation-resistant top coating of Ir, Pt, or rhodium (Rh).[1-5]

AVAILABLE FORMS, COST, AND MANUFACTURING PROCESSES

Elemental Re appears silvery-white with a metallic luster. Its usual commercial form is powder, but it can also be consolidated by pressing and resistance sintering† in a vacuum or hydrogen atmosphere. Chemically, Re is available mainly as a metal powder, perrhenic acid ($HReO_4$), or ammonium perrhenate (NH_4ReO_4). Re has become one of the ten most expensive metals following its rapid price increase during 2007 and 2008. While ammonium perrhenate was priced at 8.2 – 10.6 $/g, the metal powder was priced between 9.0 – 11.9 $/g in 2008.[6]

The two principal manufacturing processes for Re-based items are powder metallurgy (P/M) and chemical vapor deposition (CVD). Although the latter is currently the major process for deposition of Re, it is an expensive, complex, and energy intensive process. Electroplating at near-room temperature using aqueous, non-toxic bath chemistries may become a successful alternative and allow the production of uniform Re coatings on complex shapes. Electrodeposition of Re and its alloys has also recently been reviewed by Eliaz and Gileadi.[3]

Table 1. **Selected properties of rhenium. (Property range reflects different thermal conditions and suppliers of the commercially pure metal.)[1-5]**

Property	Value	Property	Value
Atomic mass	186.2 g/mol	Tensile strength	1.0–2.5 GPa
Density	21.00–21.02 g/cm^3	Yield strength	280–2350 MPa
Melting temperature	3157–3181 °C	Young's modulus	461–471 GPa
Linear thermal expansion coefficient	6.00–7.25 x 10^{-6} 1/°C	Shear modulus	155 GPa
Thermal conductivity	45–48 W/(m•K)	Strain at fracture	1–30 %
Electrical resistivity	18.7–20.0 μΩ•cm	Poisson's ratio	0.255–0.265
Fracture toughness	120–150 MPa-m$^{1/2}$	Creep-rupture strength (100 h at 2200°C)	10 MPa
Hardness	2.6–7.5 GPa	Strain hardening exponent	0.353

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Rhenium belongs to a group of metals that are difficult to produce by electrolysis of their aqueous solutions, mainly because of its very low overpotential for hydrogen evolution.[3] It has recently been reported that electroplating of pure Re was associated with low Faradaic efficiency‡ (FE ≤ 7%) and poor coating quality.[7] However, by adding a suitable nickel (Ni) salt to the bath, coatings with a Re content as high as 93 atomic percent (at.%), a FE as high as 96%, and a thickness as high as 25 µm were obtained. In addition, the Vickers hardness number (VHN) of the as-deposited coating was high: 928 ± 60 (approximately 68 Rockwell hardness C (HRC)). As the nickel ion concentration in the bath was increased, the FE and the partial current densities of both Ni and Re increased, whereas the Re content in the deposit decreased. It was proposed that the mechanism by which addition of nickel to the solution enhanced the rate of deposition of Re was through a unique type of electroless plating, in which the reducing agent was metallic Ni formed *in situ*.[7]

Rhenium was discovered in 1925 and named after the Rhine River by the German scientists who discovered the element. With an atomic number of 75, Re belongs to group VIIB and period 6 of the Periodic Table. It is located between two other refractory metals (tantalum and tungsten) and three of the platinum-group metals (osmium, iridium, and platinum). Rhenium may exist in any oxidation state between -1 and +7, but the latter (in the form of ReO_4^-) is the most stable state and can serve as a precursor for direct deposition of rhenium.

APPLICATIONS OF RHENIUM AND ITS ALLOYS

Aircraft, Aerospace, and Nuclear Reactor Applications

The major consumption of Re (approximately 70%) is as an alloying element. For example, Re is commonly used in Ni- or cobalt (Co)-based superalloys for the purpose of improving the creep strength.[6, 8] These Re superalloys provide high-temperature, creep-resistant materials for single-crystal gas turbine engine blades and other components.[4] While the second generation Ni-based alloys used in the F-15 and F-16 engines contained 3 weight percent (wt.%) Re, the third generation alloys that are used in the F-22 and F-35 engines contain approximately 6 wt.% Re.[9]

In the aircraft industry, Re is also used as a coating for face seal rotors, in air turbine starter components for gas turbine engines, as a diffusion barrier (e.g., on top of graphite), and as an alloying element in a Ni_3Al-based superalloy for vanes and in a niobium (Nb)-based alloy for advanced jet engines.[10-12] It is also used in nuclear reactors as a barrier between the uranium nitride nuclear fuel and the Nb alloy cladding.[13]

Rhenium is also an attractive material for missile propulsion and space systems. Its coatings can be used to enhance the heat resistance of carbon and graphite parts in low-oxygen environments, while avoiding carbon contamination.[4] Rhenium provides erosion resistance to components in high-temperature rocket engines and hot gas valves, lending itself to use as a liner, in conjunction with graphite or carbon-carbon structural materials, or as a pure structural material.[14] Rhenium applied in nozzles for both solid and liquid rocket engines has demonstrated tremendous advantages, allowing operation at high temperatures and gas pressures.[5] Longer lifetimes at operating temperatures of nearly 2200°C have already been proven for a combustion chamber material system composed of a Re substrate and an Ir coating (compared to a C103 Nb alloy coated with R512E fused silica). The virtual elimination of film cooling is allowed by the added thermal margin afforded by Ir-coated Re, which leads to higher performance and cleaner spacecraft environments.[2, 3, 15-17]

Rhenium greatly enhances the tensile strength and room temperature ductility of refractory metals and their alloys; thus, it is used as an alloying element of other refractory metals such as W and molybdenum (Mo).[2] For instance, W-Re alloys, with or without thoria (ThO_2), are used as electrode materials for high-temperature thermionic energy converters in space-power applications.[18] Re-Mo alloys have demonstrated superior corrosion resistance against liquid lithium (Li) and good mechanical properties, both in the base-metal and weld forms, making them potentially attractive for use as structural materials in advanced nuclear reactors.[19, 20]

Catalysts

The second highest consumption of Re (approximately 20% of the end-use) during 2008 was as a catalyst in petroleum reforming, primarily used in making lead-free, high-octane gasoline.[6] Approximately 30% of the catalysts used worldwide to convert petroleum refinery naphthas with low octane ratings into high-octane, liquid products contain Re.[21] Platinum-rhenium (Pt-Re) catalysts tolerate greater amounts of carbon formation and make it possible to operate at lower pressures and higher temperatures leading to higher yields and octane ratings.[22] In another application, Re_2O_7 is often used as a catalyst in olefin metathesis.[23] Rhenium catalysts are exceptionally resistant to poisoning by nitrogen (N), sulfur (S), and phosphorus (P), and are used for hydrogenation of fine chemicals.[22]

It has been shown that as the Re-Pt ratio increases, the catalyst lifetime increases as long as catalyzed Re reduction takes place.[24] Re-containing catalysts were found to exhibit much lower activation energies than palladium-alumina (Pd/Al_2O_3) catalysts and a drastic reduction of isomerization capability.[25] Therefore, $Re-Pt/Al_2O_3$ bimetallic catalysts are widely used in the petroleum refining industry for reforming or upgrading naphtha and have industrial application in reforming hydrocarbons for motor fuel.[24, 26] Electrodeposition of Re species at the sub-monolayer level on Pt was found to enhance the catalytic effects on formic acid and methanol electro-oxidation.[27, 28] Electro-oxidation of H_2, CO and H_2/CO mixtures on a $Pt_{75}Re_{25}$ bulk alloy has also been reported.[29] Rhenium catalysts are also increasingly used in fuel cell electrodes.[30] A rhenium-tin (Re-Sn) catalyst has been used in hydrogenation of oleic acid at low pressure with appreciable yields.[31]

Electrical Applications

Rhenium is quite attractive for electrical applications due to its high melting point, high electrical resistivity over a wide temperature range, low vapor pressure, high resistance to wear and arc erosion, and the relatively good conductivity of its surface oxides. Thus, Re-containing alloys are used in electrical contacts, mass spectrographs, electromagnets, electron tubes and targets, ionization gauges, heating elements, thermocouples, and semiconducting devices among other electrical applications.

Electrical Contacts

Alloying gold (Au) with Re has been shown to improve the hardness and high-temperature performance of Au contacts.[32] Rhenium-silver (Ag) alloys have also been used as electrical contacts in bearings for analog instruments.[4] Rhenium coatings on electrical contacts impart better performance compared to tungsten and Pt-Ruthenium (Ru) alloys.[5] Rhenium is also used as a Schottky

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barrier, which prevents the formation of the cation/anion vacancy pairs characteristic of Schottky defects.[28]

Filaments and Thermocouples

Rhenium is widely used in filaments for incandescent lamps, mass spectrographs, and ion gauges because, unlike tungsten, it is not affected by the oxidation/reduction cycle experienced in filament applications and it maintains its ductility.[2, 4, 5, 10, 13, 33] A tungsten-rhenium alloy ($W_{97}Re_3$) is used in filament-type electron emitters for instruments that measure the neutral atmospheric composition and bulk-flow velocities in the Low Earth Orbit (LEO) space environment.[34] Re-W and Re-Mo alloys are used for igniter wires in photoflash bulbs.[13]

Coatings for Electrical Applications

Rhenium coatings are used in thermo-photovoltaic (TPV) power generation systems, in which the radiator emits infrared photons from its surface to the TPV cells for conversion to electrical power. In this regard, CVD of Re whiskers was found to increase the emissivity of Mo, Nb and the Haynes 230 alloy.[35] Electrodeposited Re-selenium (Se) thin films are used as photosensitive elements in the visible range.[36] Electrodeposition of Re on silicon (Si) has been suggested for application in micro-systems.[28, 37] Electroplated Co-Ni-Re-W-P micro-arrays have been suggested for future application in magnetic micro-electro-mechanical-system (MEMS) devices.[38]

Other Electrical Applications

Thermocouples made of Re-W are used for measuring temperatures up to 2200°C. Rhenium alloys are already used for perpendicular magnetic recording (PMR) systems and have demonstrated improved properties compared to the Co-W-P alloy that was first proposed for this purpose.[39] Finally, both Re-Ru and Re-Mo alloys are superconductors at low temperatures.[2, 40]

Biomedical Applications

The radioactive isotopes of rhenium, ^{186}Re and ^{188}Re, are considered attractive candidates for radiotherapeutic applications and are widely used as labeling agents in nuclear medicine.[41] Radioactive ^{188}Re, for example, has excellent imaging properties and a relatively short biological half-life (17 hours), so it does not accumulate in the body. For instance, these radioisotopes are used as diagnostic and therapeutic agents with various ligands and their conjugates with monoclonal antibodies by means of ß-irradiation.[42, 43] In order to achieve high labeling yields, Sn^{2+} is often added.[44] The radiopharmaceutical ^{186}Re-hydroxyethylidene diphosphonate (HEDP) has been suggested for treatment of patients with painful bone metastases.[45, 46] The other isotope, ^{188}Re, has been evaluated for treatment of nonresectable/refractory liver cancer.[47]

Electrodeposition of ^{188}Re-Co on stents made of either 316L stainless steel or Nitinol shape memory alloy was applied in order to render them radioactive. It is believed that the resulting focused irradiation of cancerous tissue may improve the treatment of patients suffering from lung cancer.[48] Electrodeposition of radioactive rhenium onto stents made of either stainless steel or tantalum (Ta) has also been evaluated to prevent restenosis.[49]

Other Rhenium Coatings

Rhenium has significant potential in a variety of other coating applications. For instance, rhenium has been suggested for anti-biofouling coatings, and Re-Ru electrodeposits have been recommended as decorative coatings instead of noble metals.[40, 50] In addition, rhenium liners made by P/M and rhenium CVD coatings were suggested for the 25 mm gun tubes of the M242 automatic gun system on the Bradley Fighting Vehicle.[51] Coatings of Re and its alloys produced by low-temperature CVD have been evaluated as hard chromium (Cr) replacements.

Rhenium diboride (ReB_2) has recently been synthesized in bulk quantities via arc-melting under ambient pressure, and it was found to have a Vickers hardness higher than 40 GPa, a classification known as superhard. This material was suggested for cutting applications where the formation of carbides prevents the use of traditional materials such as diamond.[52] Bulk ReB_2 was more recently synthesized via reaction sintering under high pressure.[53] ReB_2 coatings with high corrosion resistance and wear resistance are being developed and will attract attention in the near future, e.g., as hard Cr replacements or for cutting tools.

CONCLUDING REMARKS

The unique combination of physical and chemical properties of rhenium and its alloys makes it extremely attractive as a coating in a diverse range of defense and civilian industries that include aerospace, nuclear, electrical, chemical production, and biomedical. The strong interatomic bonds and unique structure give Re its superior chemical and mechanical properties. However, these strong bonds also make the fabrication of Re time and energy intensive using current commercial methods. The use of Re and Re alloys could be facilitated in the near future with advancements in fabrication technology. Near-room temperature electroplating using non-toxic, aqueous bath chemistries has shown promise as an alternative to apply uniform Re and Re alloy coatings on complex shapes.

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*Wettability is the degree of wetting, or the ability of a liquid to maintain contact with a solid surface when the two are brought together. It is determined by a force balance between adhesive and cohesive forces and is usually defined in terms of the contact angle, which is the interior angle that a drop makes between a substrate and a tangent drawn at the intersection between the drop and the substrate.

†Resistance sintering is a process that uses an electrical current to heat and thus consolidate metals from powder form. The point where the powders are in contact creates greater resistance and requires higher temperatures to melt the powders.

‡Faradaic efficiency (FE) is the fraction of the current utilized for metal deposition (the rest is usually taken up by hydrogen evolution).

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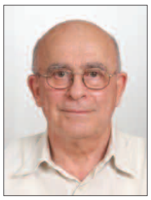

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